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Vapor-deposited alcohol glasses reveal a wide range of kinetic stability

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In situ AC nanocalorimetry was used to characterize vapor-deposited glasses of six mono- and di-alcohol molecules. Benzyl alcohol glasses with high kinetic stability and decreased heat capacity were prepared. When annealed above the glass transition temperature T_g , transformation of these glasses into the supercooled liquid took $10^{3.4}$ times longer than the supercooled liquid relaxation time (τ_α). This kinetic stability is similar to other highly stable organic glasses prepared by vapor deposition and is the first clear demonstration of an alcohol forming a stable glass. Vapor deposited glasses of five other alcohols exhibited moderate or low kinetic stability with isothermal transformation times ranging from $10^{0.7}$ to $10^2 \tau_\alpha$. This wide range of kinetic stabilities is useful for investigating the factors that control stable glass formation. Using our current results and literature data, we compare the kinetic stability of vapor deposited glasses prepared from 14 molecules and find a correlation with the value of τ_α at $1.25 T_g$. We also observe that some vapor-deposited glasses exhibit decreased heat capacity without increased kinetic stability. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4966582>]

INTRODUCTION

Physical vapor deposition can be used to prepare glasses with high kinetic stability, known as stable glasses.^{1–9} When heated, stable glasses retain their glassy structure until temperatures well above T_g .^{1–6} Additionally, if a stable glass is annealed at a temperature T_{anneal} above T_g , the transformation into the supercooled liquid can take 10^5 times longer than the supercooled liquid structural relaxation time ($\tau_\alpha(T_{\text{anneal}})$).^{1,6–9} For comparison, a liquid-cooled glass transforms in roughly $1 \tau_\alpha$ in such an annealing experiment. The formation of stable glasses is thought to be enabled by enhanced surface mobility of molecules at temperatures below T_g .^{1,10,11} During deposition at temperatures near $\sim 0.8 T_g$, molecules at the surface of a growing film have enough mobility to find low energy packing configurations. After being buried by further deposition, these configurations have high barriers to rearrangement, leading to the high kinetic stability observed in experiments. When compared to liquid-cooled glasses, stable glasses can also have lower enthalpy,^{1–4} lower molar volume,^{1,12–15} and lower heat capacity.^{6,16} Since their discovery in 2007, stable glasses have been prepared from 28 organic molecules.^{1,2,6,7,9,12,14,15,17–23} The properties of stable glasses have also been qualitatively replicated in simulations.^{24–29}

Despite the many molecules that have been used to prepare stable glasses by vapor deposition, there have been a few cases in which stable glass formation has not occurred in the expected range of substrate temperatures. Some molecules crystallize too readily to prepare vapor-deposited glasses.²⁰

Other molecules, when vapor deposited using conditions expected to yield stable glasses, yield glasses with low kinetic stability.^{30–33} For this paper, it is useful to define a “stable glass forming ability” which is analogous to glass forming ability. While glass forming ability might be assessed by determining whether or not crystallization occurs when cooling at a given rate, stable glass forming ability can be assessed by comparing the kinetic stability of vapor-deposited glasses prepared at a given deposition rate.

One proposed indicator of stable glass forming ability is supercooled liquid fragility. There are many ways to characterize how the temperature-dependent dynamics of a liquid deviate from Arrhenius behavior, but fragility is most often expressed by the fragility index m ,

$$m = \left. \frac{d \log(\tau_\alpha)}{dT_g/T} \right|_{T_g}. \quad (1)$$

Yu and Samwer deposited glasses of a metallic alloy with a low value of m and reported enhanced kinetic stability.³⁰ However, the transformation temperature upon heating was only about $1.02 T_g$ in comparison to the value of $1.05 T_g$ that has often been observed for stable glasses of organic molecules.^{6,9,19,20,23,34–36} Yu and Samwer reported a moderate correlation between the transformation temperature of the vapor-deposited glasses and the fragility index m of the corresponding supercooled liquid. Molecules with larger values of m generally produced glasses with higher transformation temperatures relative to T_g .³⁰ At about the same time, Ishii and co-workers found a correlation between m and the ability to form dense glasses via physical vapor deposition. In particular, two molecules with relatively low m , ethylcyclohexane ($m = 57$) and butyronitrile ($m = 56$), were

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reported not to form dense glasses.¹³ Given the common correlation between kinetic stability and density in stable glasses, one might expect based upon this that low m molecules would not be able to form stable glasses.³⁷ However, it was later established that vapor-deposited glasses of methyl-*m*-toluate ($m = 60$) and ethylcyclohexane ($m = 57$) can exhibit high kinetic stability.^{7,9,22} At present, glasses with high kinetic stability have been prepared from molecules with m ranging from very high ($m = 146$)²⁰ to moderately low ($m = 57$).^{9,22} Thus it seems unlikely that m is a good predictor of stable glass forming ability in this range. However, it has been argued that substances with very low values of m (approaching the strong liquid limit of $m = 16$) will not be able to form stable glasses.³⁸

Molecules with extensive hydrogen bonding, particularly those with hydroxyl groups, may have difficulty forming stable glasses based upon the information presently available. Wübbenhorst and co-workers have prepared vapor-deposited glasses of glycerol and two longer chain polyols. The deposition of these molecules yields glasses that, when heated, produce liquids with very interesting properties, including longer relaxation times and increased orientational order in comparison to the ordinary supercooled liquid.^{31,32} However, the as-deposited glasses do not seem to exhibit substantial enhanced kinetic stability. Sepúlveda and co-workers have prepared vapor-deposited glasses of water using a wide range of substrate temperatures but did not report stable glass formation.³³ While Souda prepared n-propanol, ethanol, and methanol glasses by vapor deposition, the substrate temperature was low enough that no conclusive statement can be made about stable glass formation.³⁹ Thus, at present there is no clear example of an alcohol that can be vapor-deposited into a glass with high kinetic stability. Recent experiments by Chen and co-workers provide a reason why it may be difficult to form stable glasses from alcohols.⁴⁰ They reported that the surface diffusion coefficients at T_g for three polyols (sorbitol, maltitol, and maltose) are at least four orders of magnitude smaller than for organic molecules with no hydrogen bonding. This suggests that the surface mobility needed during deposition to achieve efficient packing may not be available for such extensively hydrogen bonded systems.

In the current work, we survey the stable glass forming ability of alcohols by vapor-depositing glasses of six alcohols and characterizing them with AC nanocalorimetry. The molecules we have selected are shown in Figure 1 and include mono- and di-alcohols, aromatic and aliphatic molecules, and short and long alkyl chains. One of the molecules, benzyl alcohol, has the additional feature of being a structural analog of ethylbenzene, a well-studied stable glass forming molecule.^{3,5,12,34} We use two experiments to test the kinetic stability of vapor-deposited glasses. We measure the transformation temperature of the glass during a temperature ramping experiment and compare it to T_g . For stable glasses, this transformation temperature is often 5% higher than T_g .^{6,9,19,20,23,34–36} In a second test, we perform isothermal annealing experiments at temperatures above T_g and use the reversing heat capacity to track the transformation of the as-deposited glass into the supercooled liquid.

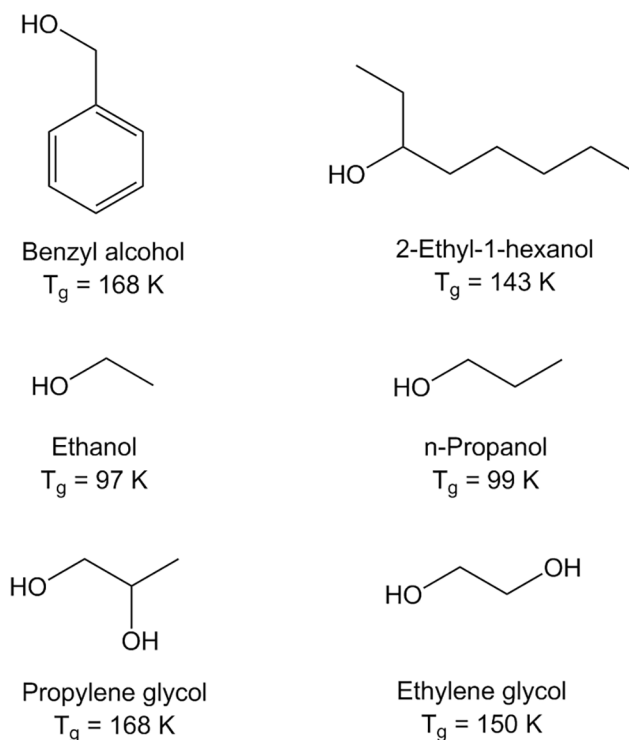


FIG. 1. Molecules tested in this study for the ability to form stable glasses using physical vapor deposition.

We observe a wide range of stable glass forming ability in our survey of vapor-deposited alcohols. We prepared glasses with high kinetic stability from benzyl alcohol, which is the first clear demonstration of an alcohol forming a stable glass. Glasses of 2-ethyl-1-hexanol and ethanol exhibited at most moderate kinetic stability, and we were not able to prepare glasses with enhanced kinetic stability from ethylene glycol, n-propanol, or propylene glycol. We combine our measured kinetic stability results with data from 8 previously studied stable glass formers to investigate factors that may correlate with stable glass forming ability.^{6,7,9,34,36,41,42} We find that stable glass forming ability correlates reasonably well with the supercooled liquid τ_α at $1.25 T_g$; this value is a measure of liquid fragility and our consideration was inspired by the recent observation that a closely related quantity correlates with the surface diffusion coefficient at T_g .⁴⁰ Two more commonly used measures of fragility (m and $F_{1/2}$) do not correlate as well with stable glass forming ability. Vapor-deposited glasses of benzyl alcohol and 2-ethyl-1-hexanol were observed to have decreased heat capacities relative to the liquid-cooled glasses. At some deposition temperatures, vapor-deposited glasses of 2-ethyl-1-hexanol exhibit decreased heat capacity without having increased kinetic stability.

EXPERIMENTAL

Materials

Benzyl alcohol with 99.8% purity, 2-ethyl-1-hexanol with $\geq 99.6\%$ purity, ethylene glycol with $\geq 99.8\%$ purity, and propylene glycol with $\geq 99.5\%$ purity were all purchased from Sigma Aldrich and used without further purification

in experiments at the University of Wisconsin – Madison. Ethanol with 99.8% purity was purchased from Carl Roth and n-propanol with 99.5% purity was purchased from Sigma Aldrich. The molecules were used without further purification in experiments at the University of Rostock. The T_g values in Figure 1 for 2-ethyl-1-hexanol, ethanol, n-propanol, propylene glycol, and ethylene glycol correspond to $\tau_\alpha = 100$ s from dielectric spectroscopy data.^{43–47} Dielectric experiments have not been reported for benzyl alcohol; the listed value was obtained from differential scanning calorimetry measurements at 5 K/min.^{48,49}

Apparatus

The vacuum deposition chambers and AC nanocalorimetry instrumentation at the University of Wisconsin – Madison and at the University of Rostock have been described in detail previously.^{34,36,50} The apparatuses are similar and we will give a general description that applies to both laboratories. Sample deposition and measurement took place inside an ultra-high vacuum chamber pumped by a turbo pump in series with a dry backing pump. The typical base pressure of both chambers is 10^{-9} mbar. Molecules are introduced into the chamber for deposition by a fine leak valve. The relative deposition rate is monitored by the ion gauge pressure. AC nanocalorimetry devices (chip calorimeters produced by Xensor Integration bv, The Netherlands) were held in copper housings attached to a cryostat. The copper housings contained a resistive thermometer device and a cartridge heater to allow for temperature control. A thermal oscillation is created on the nanocalorimeter membrane by an AC voltage applied to the device heater by the internal oscillator of a Signal Recovery 7265 DSP (Digital Signal Processing) lock-in amplifier. We measure a differential thermopile signal between a nanocalorimeter containing a sample and an empty reference device. We subtract a background measurement of the two empty devices to account for the fact that both devices are not completely identical. The resulting differential signal is proportional to the reversing heat capacity of the films. No strain correction was applied in these experiments as the films are sufficiently thin to make the correction negligible.^{6,20} Except for one experiment in which a wide frequency range was utilized, all reversing heat capacity measurements reported here were measured at 20 Hz.

Experiments

The film thicknesses at the University of Wisconsin – Madison were estimated by comparing our deposition to previous tandem AC nanocalorimetry and ellipsometry measurements of methyl-*m*-toluate films.³⁶ At the University of Rostock, film thicknesses were estimated using previously reported finite element modeling calculations.⁵⁰ In each case, we deposited films that corresponded to particular heat capacity changes (rather than particular thicknesses) on the sensors. Since the deposited alcohols have somewhat different volumetric heat capacities, this results in (at most) a 26% error in the reported thickness. The effect of this error on transformation times is much smaller

than other uncertainties for the transformation times reported in Figures 6 and 8. Thus, we will only report approximate glass thicknesses and we did not adjust the transformation times for small differences in film thicknesses. Deposition rates calculated from the deposition time and thickness ranged from 0.1 to 0.3 nm/s. The films for temperature ramping experiments were approximately 250 nm thick. The films for quasi-isothermal annealing experiments were approximately 590 nm thick and were deposited on top of a 250 nm layer of liquid-cooled glass. The use of such a bilayer geometry ensures that there will be two growth fronts if the vapor-deposited glass transforms via front propagation.^{36,51}

The temperature of the AC nanocalorimetry devices was calibrated by measuring the alpha relaxation of supercooled liquids and comparing to the literature measurements as described previously.^{9,36,50} With this procedure, the absolute temperature is known to ± 1 K. During temperature ramping experiments, a 5 K/min heating and cooling rate was used at the University of Wisconsin – Madison, while a 0.67 K/min heating rate was used at the University of Rostock. At most, the T_{onset}/T_g values for ethanol and n-propanol reported in Figure 5(a) are 0.013 lower than they would be if 5 K/min were used at Rostock. This effect is small enough that it does not affect our qualitative evaluation of stable glass forming ability. The quantitative evaluation of stable glass forming ability was done using quasi-isothermal annealing experiments, which are not affected by heating rate. (These annealing experiments are quasi-isothermal because of the ~ 0.3 K temperature oscillation of the AC calorimetry technique.) During the temperature jump prior to the quasi-isothermal annealing experiments, the temperature overshoot was 0.1 K or less, and subsequently the temperature was constant to ± 0.1 K. The quasi-isothermal annealing temperatures utilized were 174 K for benzyl alcohol, 146 K for 2-ethyl-1-hexanol, 97 K for ethanol, 99 K for n-propanol, 151 K for ethylene glycol, and 167 K for propylene glycol.

Data analysis

For comparisons shown below (Figure 8), we calculated isothermal transformation times for stable glass forming molecules from prior publications. Stable glasses transform via propagating fronts,^{29,36,51–55} and the front velocity has been measured as a function of annealing temperature for many molecules.^{6,7,9,34,36,41,42} All of these data was obtained using deposition rates near 0.2 nm/s and the substrate temperature that maximizes kinetic stability. We use these data to calculate the transformation times expected for 590 nm stable glass films with two transformation fronts (i.e., the time required for one front to propagate 295 nm), since we used bilayer films in our current experiments. We calculate the transformation times (ratioed to τ_α) at an annealing temperature that corresponds to $\tau_\alpha = 50$ s. Consistent with the calculation described above, for all but one of the known stable glass formers in Figures 7 and 8, a single transformation front has been shown to propagate at least 400 nm before the intervention of a bulk transformation mechanism. For stable glasses of N, N'-bis(3-methylphenyl)-N, N'-diphenylbenzidine (also known as TPD) experiments on thicker films have not been published,

but we expect the transformation fronts of TPD will also propagate at least 295 nm during the transformation of thick films.

For comparisons shown below (Figures 7 and 8), we compiled supercooled liquid dynamics data for the six alcohols studied here and for eight known stable glass formers. Most of this data is from dielectric spectroscopy and NMR experiments that directly report τ_α . In some cases, viscosity data were used to calculate $\tau_\alpha = \eta/G_\infty$ with $G_\infty = 0.5$ GPa for ethylcyclohexane,⁵⁶ $G_\infty = 0.31$ GPa for indomethacin, $G_\infty = 0.159$ GPa for TNB, and $G_\infty = 81.1$ MPa for ethylbenzene.³⁷ The values of G_∞ for indomethacin and TNB were chosen such that viscosity and dielectric measurements match in the temperature region where the measurements overlap. The G_∞ values for ethylcyclohexane and ethylbenzene have been used previously to calculate τ_α from viscosity data.^{37,56} We used the Wirtz equation ($\tau = 4\pi\eta^3/6 kT$) to calculate τ_α from the benzyl alcohol viscosity data,^{57,58} assuming a molecular radius of 0.31 nm.

We measured τ_α deep in the supercooled liquid of benzyl alcohol using AC nanocalorimetry measurements that spanned the frequency range of 4 Hz–4 kHz.

We determined T_g , m , $T_{1/2}$, and also $\log(\tau_\alpha)$ at $1.25 T_g$ from the compiled data sets. We used a Stickel analysis to determine the characteristic temperature T_B for each system.^{59,60} Then, we determined VTF fits (Equation (2)) to the data below T_B by first setting T_0 by linearizing $\log(\tau_\alpha)$ vs $1/(T - T_0)$,⁶¹

$$\log(\tau_\alpha) = A + \frac{B}{T - T_0}. \quad (2)$$

The VTF parameters were then used to derive T_g (where $\tau_\alpha = 100$ s) and m , as described by Chen and Richert.³⁷ We also estimated m by two other methods, determining the slope of the lowest temperature data and performing a linear fit to the derivative of $\log(\tau_\alpha)$ vs T_g/T and extrapolating to T_g . The m values plotted in Figure 8(a) are averages of these 3 methods. We determined the values of $T_{1/2}$ and $\log(\tau_\alpha)$ at $1.25 T_g$ by interpolating the available data when possible, and extrapolating when necessary.

RESULTS

Temperature ramping experiments

As shown in Figure 2, temperature ramping AC nanocalorimetry experiments demonstrate that benzyl alcohol can form stable glasses via vapor deposition. The as-deposited glasses maintain their glassy heat capacity until temperatures as high as 13 K above T_g ($1.08 T_g$) before transforming into the supercooled liquid. This significantly increased onset temperature is an indication of the enhanced kinetic stability that defines a stable glass.^{1–6} The benzyl alcohol stable glasses also have lower reversing heat capacities than the liquid-cooled glass. Reduced heat capacity is a feature that has been observed previously in many other stable glasses.^{6,8,9,16,20,23,34,36}

The AC calorimetry measurements are made by applying an oscillating heat input to the sample at a frequency of 20 Hz, and measuring the amplitude of the 20 Hz temperature oscillation; the amplitude is used to obtain the reversing

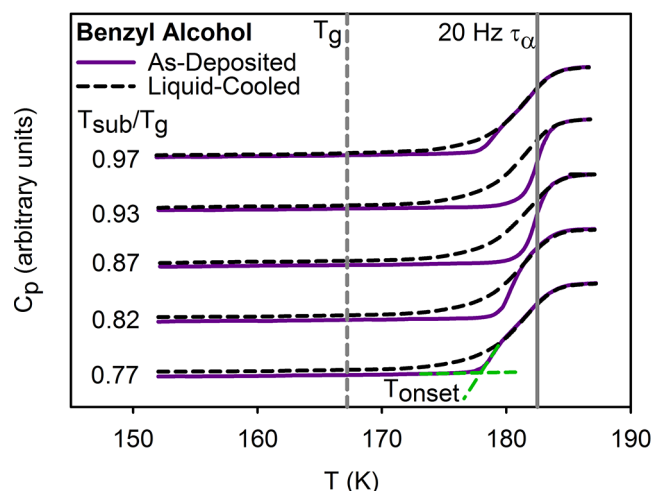


FIG. 2. Temperature ramping AC nanocalorimetry experiments of benzyl alcohol glasses. Solid purple curves are as-deposited glasses prepared by physical vapor deposition. Dashed black curves are glasses prepared by cooling the supercooled liquid. The green dashed tangent lines demonstrate the determination of T_{onset} . The as-deposited glasses exhibit significantly increased onset temperatures and decreased heat capacity, features that have been previously observed in stable glasses. The curves for different substrate temperatures have been vertically shifted. The noted value of T_g comes from 5 K/min DSC measurements.^{48,49} The 20 Hz τ_α value comes from the minimum in the phase data from AC nanocalorimetry measurements.

heat capacity. The liquid-cooled glass (dashed black lines) shows an increase in the reversing heat capacity value at the temperature when the structural relaxation occurs at 20 Hz. At lower temperatures, the structural relaxation process is too slow to adsorb energy from the 20 Hz heating, and the reversing heat capacity is low. As the temperature increases, a growing fraction of molecules undergo structural relaxation at a frequency of 20 Hz and the reversing heat capacity increases. Eventually the value of the reversing heat capacity levels off at a temperature where the structural relaxation of all molecules is faster than 20 Hz. The transformation of the vapor-deposited glass begins at the onset temperature (T_{onset}) where the reversing heat capacity deviates from the nearly flat response of the glass. The tangent lines drawn for the 0.77 T_{sub}/T_g glass provide an example of how T_{onset} is determined. We will compare the features of the temperature ramping experiments for all six alcohols in Figure 5.

Vapor-deposited glasses of 2-ethyl-1-hexanol exhibit modestly enhanced kinetic stability when deposited near T_g . These temperature ramping experiments are shown in Figure 3. Glasses deposited at $0.96 T_g$ and $0.91 T_g$ have onset temperatures that are, at most, 5 K higher than T_g . This is a smaller increase (up to $1.036 T_g$) compared to the $1.08 T_g$ value observed for the most stable benzyl alcohol glasses. All the vapor-deposited glasses of 2-ethyl-1-hexanol exhibit decreased reversing heat capacities compared to the liquid-cooled glass. The heat capacity of vapor-deposited glasses with $T_{\text{sub}}/T_g = 0.86$ and 0.80 goes through a small step before T_g which is a feature of an unstable glass. The combination of low stability and a lower reversing heat capacity is surprising and discussed below.

As shown in Figure 4, the vapor-deposited glasses of ethanol, n-propanol, ethylene glycol, and propylene glycol

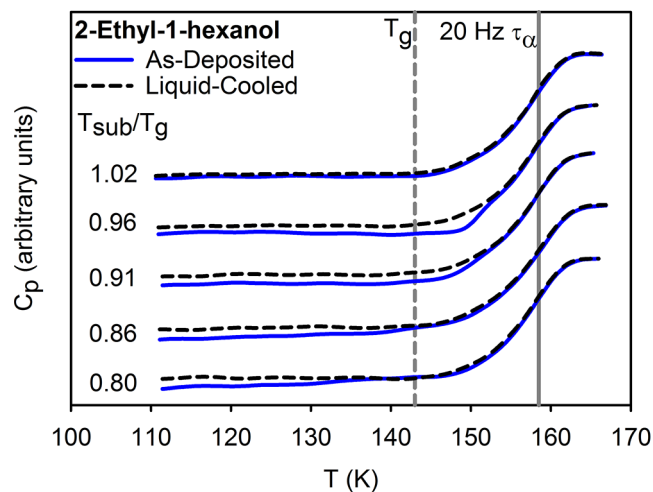


FIG. 3. Temperature ramping AC nanocalorimetry experiments of 2-ethyl-1-hexanol glasses. Solid blue curves are as-deposited glasses prepared by physical vapor deposition. Dashed black curves are liquid-cooled glasses. 2-ethyl-1-hexanol glasses deposited at $0.96 T_g$ and $0.91 T_g$ have moderately enhanced kinetic stability but glasses prepared with lower substrate temperatures do not. The curves for different substrate temperatures have been vertically shifted. The noted value of T_g is the temperature when $\tau_\alpha = 100$ s.⁴³

exhibit little to no enhanced kinetic stability. The vapor-deposited glasses of ethanol, ethylene glycol, and propylene glycol have reversing heat capacities that are slightly lower than the liquid-cooled glass, but the magnitude of the decrease is much less than for benzyl alcohol and 2-ethyl-1-hexanol. The reversing heat capacities of the as-deposited n-propanol glasses are very similar to that of the liquid-cooled glass, and instrumental noise does not allow us to quantify any slight differences.

The onset temperatures of the as-deposited glasses of these six alcohols are compared in Figure 5(a) as a function of the substrate temperature during deposition. Glasses that have a T_{onset}/T_g value greater than 1 maintain their glassy

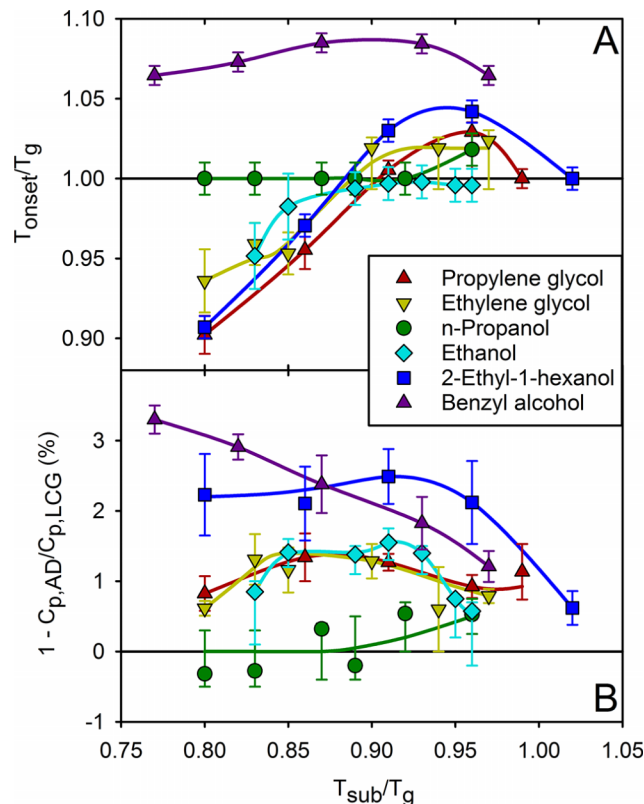


FIG. 5. Comparison of the properties of vapor-deposited glasses of six alcohols. (a) T_{onset}/T_g vs normalized substrate temperature during deposition (T_{sub}/T_g). Error bars represent the uncertainty in the observed T_{onset} and in the absolute temperature. (b) Reversing heat capacity decrease of vapor-deposited glasses compared to liquid-cooled glasses as a function of substrate temperature during deposition. The heat capacity decrease is determined in the glassy region before any onset temperature.

properties to temperatures higher than T_g and can be said to have enhanced kinetic stability.¹⁻⁶ Vapor-deposited glasses of benzyl alcohol have a maximum T_{onset}/T_g of 1.08 and exhibit increased onset temperatures from $T_{\text{sub}}/T_g = 0.97$ to below

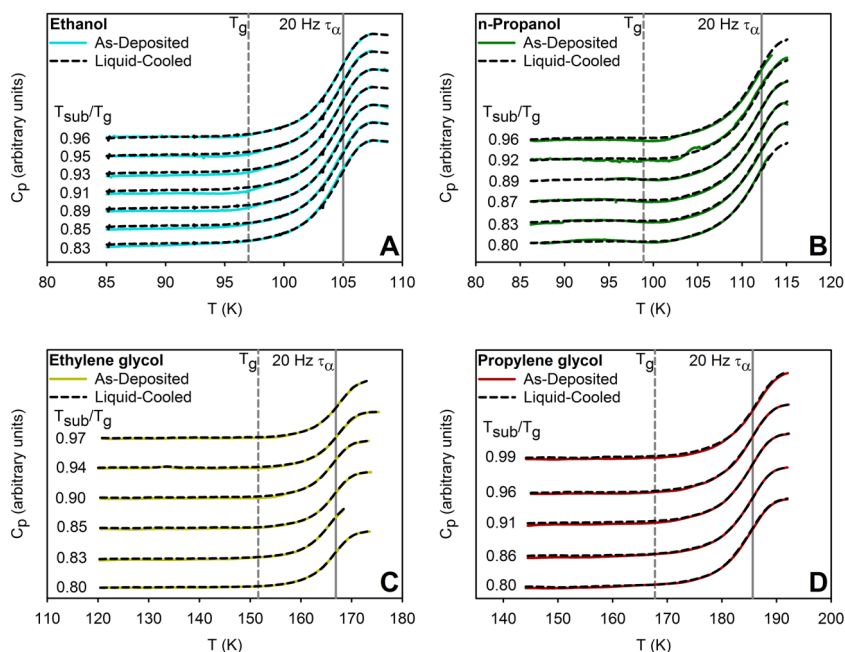


FIG. 4. Temperature ramping AC nanocalorimetry experiments of ethanol (a), n-propanol (b), ethylene glycol (c), and propylene glycol (d) glasses. The solid colored lines are as-deposited (AD) glasses while the dashed black curves are liquid-cooled glasses. None of the vapor-deposited glasses show enhanced kinetic stability. The curves for different substrate temperatures have been vertically shifted. The noted value of T_g is the temperature when $\tau_\alpha = 100$ s.⁴³⁻⁴⁷

$T_{\text{sub}}/T_g = 0.77$. This behavior is typical of previously studied stable glasses. 2-ethyl-1-hexanol, propylene glycol, ethylene glycol, and n-propanol have elevated onset temperatures when deposited just below T_g , but these onset temperatures are relatively low. When 2-ethyl-1-hexanol, propylene glycol, ethylene glycol, and ethanol are deposited at temperatures below $0.90 T_g$, they make unstable glasses as evidenced by changes in their glassy heat capacity at temperatures below T_g . In contrast, for known stable glass forming molecules, the phenomenon of preparing an unstable glass does not occur unless the glass is deposited at temperatures below $0.70 T_g$.^{6,9,34} The vapor-deposited glasses of n-propanol had reversing heat capacity traces that were very similar to the liquid-cooled glass. Because of this small difference and instrument noise, we were unable to observe any unstable glass behavior if it exists for this molecule.

Figure 5(b) shows the decrease in the reversing heat capacity for vapor-deposited glasses of the six alcohols, relative to the liquid-cooled glasses. Decreased heat capacity is a property that has been observed in many stable glasses.^{6,8,9,16,20,23,34,36} Vapor-deposited glasses of benzyl alcohol have heat capacities that are 1%–3% lower than a liquid-cooled glass depending on substrate temperature; this range and temperature dependence are similar to what has been seen in known stable glasses. Figure 5 also illustrates the interesting result of unstable glasses with decreased reversing heat capacity. 2-ethyl-1-hexanol glasses deposited below $0.90 T_g$ provide the best examples of this phenomenon.

Quasi isothermal annealing experiments

We performed quasi-isothermal annealing experiments to quantify the kinetic stability of the vapor-deposited alcohols, with the results shown in Figure 6. During annealing, the reversing heat capacity of the sample increases as it transforms from glass to supercooled liquid. The “% liquid” value is obtained by normalizing the heat capacity increase with respect to the value of the supercooled liquid. Thus during the annealing, the % liquid increases as the sample transforms and levels off once the transformation is complete. We have also normalized the time axis by dividing by τ_α of the supercooled liquid at the annealing temperature.

The six alcohols shown in Figure 6 exhibit a wide range of isothermal transformation times. The transformation times of the propylene glycol, ethylene glycol, and n-propanol glasses are less than $10 \tau_\alpha$ and we characterize these glasses as having low kinetic stability. For comparison, a liquid-cooled glass should transform in about $1 \tau_\alpha$ under the conditions of these experiments. The vapor-deposited glasses of ethanol and 2-ethyl-1-hexanol have transformation times between 10 and $1000 \tau_\alpha$, and exhibit moderate kinetic stability. The vapor-deposited glass of benzyl alcohol has a transformation time greater than $1000 \tau_\alpha$. Known stable glasses have transformation times that range from $\log(t_{\text{transformation}}/\tau_\alpha) = 3$ to $\log(t_{\text{transformation}}/\tau_\alpha) = 5$,^{6,7,9,34,36,41,42} and we designate the benzyl alcohol data as showing high kinetic stability. The precise transformation time cutoffs for low, moderate, and high kinetic stability are arbitrary, but these classifications will facilitate further discussion.

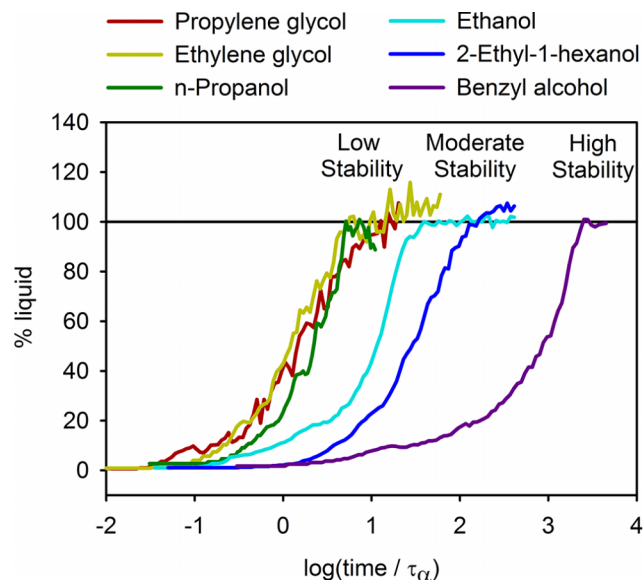


FIG. 6. Isothermal transformation kinetics of vapor-deposited glasses of six alcohols. For each alcohol, vapor-deposited glasses were prepared at the substrate temperature that yielded the highest T_{onset} and then heated to $T_{\text{anneal}} \geq T_g$. The vertical axis represents the change in the reversing heat capacity signal from the initial glassy value to the supercooled liquid value. The annealing time is normalized by τ_α of the supercooled liquid at the annealing temperature. Data have been smoothed for clarity.

DISCUSSION

The role of the hydroxyl group in stable glass formation

We have prepared stable glasses of benzyl alcohol and this is the first clear example of an alcohol that can form a stable glass. As discussed in the Introduction, previous studies of vapor deposition of alcohols were inconclusive.^{31–33,39,40} The high onset temperatures and long transformation times for vapor-deposited glasses of benzyl alcohol (Figures 2 and 6) unambiguously show the high kinetic stability that defines a stable glass. The proposed mechanism of stable glass formation is that molecules have enhanced surface mobility during deposition and thus are able to reach packing arrangements that have high barriers to relaxation once the molecule is buried by further deposition.^{1,10,11} Enhanced surface mobility has been observed in many experiments^{1,11,62–64} and simulations,^{65–68} and has been described by theory.^{69,70} Because it can form a stable glass, we expect that benzyl alcohol has significantly enhanced surface mobility.

In contrast, 2-ethyl-1-hexanol, ethanol, n-propanol, ethylene glycol, and propylene glycol do not form stable glasses and we speculate that this occurs because their surface mobility is too low. During vapor deposition, these molecules apparently sample configurations only slowly and do not find low energy configurations with high barriers to rearrangement. If this view is correct, then we expect that highly stable glasses of molecules like 2-ethyl-1-hexanol could be prepared if we use extremely slow deposition rates; we plan to test this prediction in further experiments. The temperature dependence of the onset temperature for the five alcohols that do not form stable glasses is consistent with limited surface mobility during deposition. For these

five molecules, the optimal deposition temperature is around $0.95 T_g$ as seen in Figure 5(a) for 2-ethyl-1-hexanol, ethanol, n-propanol, ethylene glycol, and propylene glycol. This is much higher than the optimum substrate temperature of $\sim 0.85 T_g$ that is typically observed in stable glass forming molecules.^{6,15,21,23,71} The optimal substrate temperature is the result of the competition between the temperature dependence of the surface mobility and the energy levels of available configurations, where a low energy level often results in a high barrier to rearrangement.^{1,10} At higher deposition temperatures, molecules have sufficient surface mobility to sample configurations, but the available configurations have lower barriers to rearrangement. At lower deposition temperatures there are configurations with much higher barriers, but the molecules do not have enough mobility to reach these configurations during the time that they remain near the surface. If a glass has limited surface mobility, we would expect the optimal deposition temperature to be higher than for stable glass formers.

Our hypothesis of limited surface mobility for the five alcohols that do not form stable glasses is related to a recent study of the effect of hydrogen bonding on diffusion at the surface of glasses. Stable glass forming molecules with no hydrogen bonding have surface diffusion coefficients that can exceed the bulk diffusion coefficient as much as 8 orders of magnitude at T_g .^{11,63,64} For a molecule that is only subject to van-der-Waals forces, it is natural to imagine that the reduction of neighbors at the surface significantly reduces the barriers to motion. Chen and co-workers discovered that the surface diffusion of polyols at T_g is at least 4 orders of magnitude slower than for similarly sized non-hydrogen-bonding molecules.^{40,64,72} They hypothesize that polyol molecules restructure at the surface such that they maintain a high number of hydrogen bonds despite losing some neighbors. Because of these strong intermolecular interactions, the barriers to motion at the surface would still be relatively high.⁴⁰ Based on the work of Chen and co-workers, one would predict that molecules with extensive hydrogen bonding would not have the surface mobility required to form highly stable glasses. (In this paragraph, we have assumed that high rates of surface diffusion are associated with high rates of configurational sampling and this assumption may need to be carefully examined.)

In light of the work of Chen and co-workers, it is natural to ask whether the five alcohols that fail to form stable glasses exhibit more extensive hydrogen bonding than benzyl alcohol. The literature indicates that this is likely to be the case. The two diol liquids (propylene glycol and ethylene glycol) are understood to have hydrogen bonding clusters or hydrogen bonded networks.^{73–78} Extensive intermolecular hydrogen bonding is observed in simulations of these liquids^{73,76,77} and presumably has a major influence on the liquid dynamics.^{74,75,78} n-propanol and 2-ethyl-1-hexanol exhibit Debye peaks in the dielectric spectra of the supercooled liquids.^{43,45} This strong peak that occurs at frequencies below the alpha process for mono alcohols is understood to report the dynamics of supramolecular structures held together by intermolecular hydrogen bonding.⁷⁹ Various experiments support the picture of hydrogen bonded structures in

n-propanol⁸⁰ and 2-ethyl-1-hexanol,^{81,82} while simulations of liquid n-propanol also predict hydrogen bonded clusters.⁸³ It is not yet clear if supercooled ethanol exhibits a Debye peak,⁴⁴ but experimental and computational works agree that the structure of liquid ethanol is dominated by hydrogen bonded clusters.^{80,83,84} There is not yet a consensus on the structure of liquid benzyl alcohol. Some authors have presented evidence of extended structures,^{85,86} but others have claimed that benzyl alcohol only forms dimers⁸⁷ or that the interaction between aromatic groups is responsible for any cluster since only a small fraction of the OH groups participates in intermolecular hydrogen bonding.⁸⁸ While there is not a clear answer from the literature, if one considers the steric size of the phenyl group, it is plausible that benzyl alcohol contains smaller hydrogen bonded clusters or fewer clusters compared to the five alcohols that fail to form stable glasses. Based on the experiments in this study, we hypothesize that benzyl alcohol glasses exhibit significantly enhanced surface mobility while the five other alcohols do not. The above literature concerning intermolecular hydrogen bonding for the six molecules in this work and the recent report from Chen and co-workers support our hypothesis.

Vapor-deposited glass kinetic stability and supercooled liquid dynamics

As discussed in the Introduction, there have been several attempts to connect stable glass forming ability with supercooled liquid fragility.^{13,30,37,38} Our data on vapor-deposited alcohol glasses considerably expand the range of systems that can be evaluated and so we further consider this possible connection. We have compiled transformation times from annealing experiments for the vapor-deposited alcohols studied here and for 8 previously studied stable glass forming molecules. We expand the earlier discussion of the role of fragility by considering additional measures of fragility beyond “*m*.”

Figure 7 presents $\log(\tau_\alpha)$ as a function of scaled inverse temperature for the 14 liquids for which we have kinetic stability data for the vapor-deposited glasses. The values of τ_α come from dielectric spectroscopy, NMR, and viscosity literature.^{37,42–47,56,89–103} Our procedure for calculating τ_α from viscosity data can be found in the section titled “Experimental.” In the case of benzyl alcohol, AC calorimetry measurements were used to determine τ_α for values between 10^{-5} s and 10^{-1} s.

We utilized three measures of supercooled liquid fragility for the comparison with vapor-deposited glass stability. The “*m*” fragility parameter, defined by Equation (1), is equal to the slope of the data at T_g/T . We also utilized the $F_{1/2}$ measure of fragility proposed by Angell and co-workers,¹⁰⁴

$$F_{1/2} = 2 \frac{T_g}{T_{1/2}} - 1, \quad (3)$$

where $\tau_\alpha = 100$ s at T_g and $\tau_\alpha = 10^{-6}$ s at $T_{1/2}$.

$T_{1/2}$ can be identified in Figure 7 from the solid horizontal line. Similar to *m*, larger values of $F_{1/2}$ indicate greater deviation from the strong liquid limit. As a third measure of fragility, we consider $\log(\tau_\alpha)$ at $1.25 T_g$. The value of $\log(\tau_\alpha)$

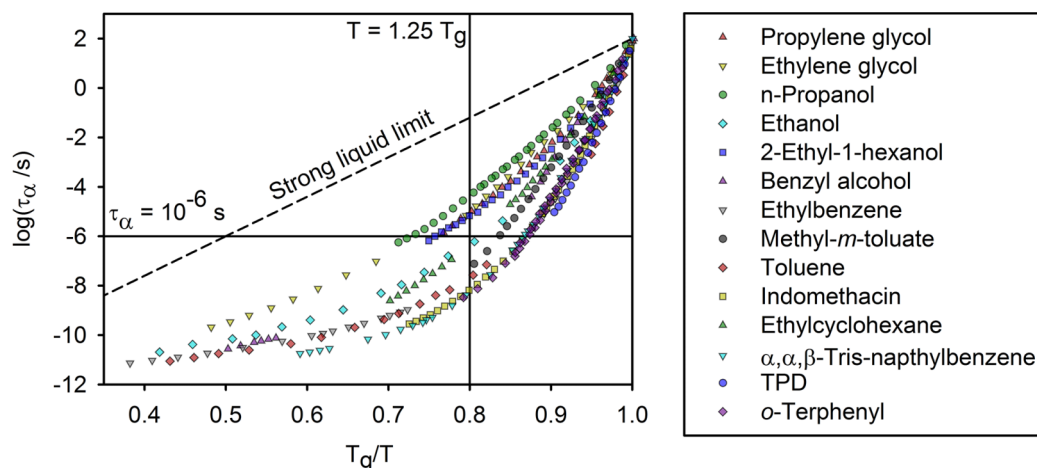


FIG. 7. Supercooled liquid dynamic data for 14 glass-forming liquids, for comparison with kinetic stability of vapor-deposited glasses. The fragility index m can be evaluated by taking the slope at $T_g/T = 1$. The $F_{1/2}$ measure of fragility is related to the value of T_g/T when $\tau_\alpha = 10^{-6} \text{ s}$ (horizontal solid line). Smaller values of $\log(\tau_\alpha)$ at $1.25 T_g$ are further from the strong liquid limit and thus represent greater fragility; this value of $\log(\tau_\alpha)$ can be identified from the vertical solid line. Data sources given in text. TPD is the acronym used for N, N'-bis(3-methylphenyl)-N, N'-diphenylbenzidine.

at $1.25 T_g$ is a measure of fragility in that smaller values represent a greater deviation from the Arrhenius behavior of strong liquids, and thus greater fragility. Our choice of the $\log(\tau_\alpha)$ at $1.25 T_g$ is inspired by the recent paper from Chen and co-workers.⁴⁰ They have found that the surface diffusion constant at T_g of glass formers correlates well with $\log(\eta)$ at $1.25 T_g$. For consistency with the other two fragility measures, we elected to use τ_α rather than η , but since these quantities are nearly proportional to each other in supercooled liquids, we do not think that this would have a significant impact on our conclusions.

In Figure 8, the transformation times for vapor-deposited glasses are plotted versus the three measures of supercooled liquid fragility. Transformation times for the six alcohols come from Figure 6 while published data are used for the other molecules. In Figure 8(a) we observe a poor correlation

between stable glass forming ability and m (Equation (1)). In particular, note that m values near 55 are associated with a range of transformation times that covers more than 3 orders of magnitude. Given the lack of correlation in previously published comparisons utilizing the m fragility parameter, this result was expected.^{7,9,22,30} In Figure 8(b) we plot the normalized transformation times as a function of the $F_{1/2}$ measure of fragility. We consider that this correlation is modestly improved in comparison to the m fragility parameter. Finally, in Figure 8(c), we observe that $\log(\tau_\alpha)$ at $1.25 T_g$ correlates reasonably well with the stable glass forming ability. The different measures of fragility compared in Figure 8 emphasize deviations from strong liquid behavior in different temperature regimes. One might expect that m would best correlate with the stable glass forming ability because it is evaluated closest to the temperature range where vapor

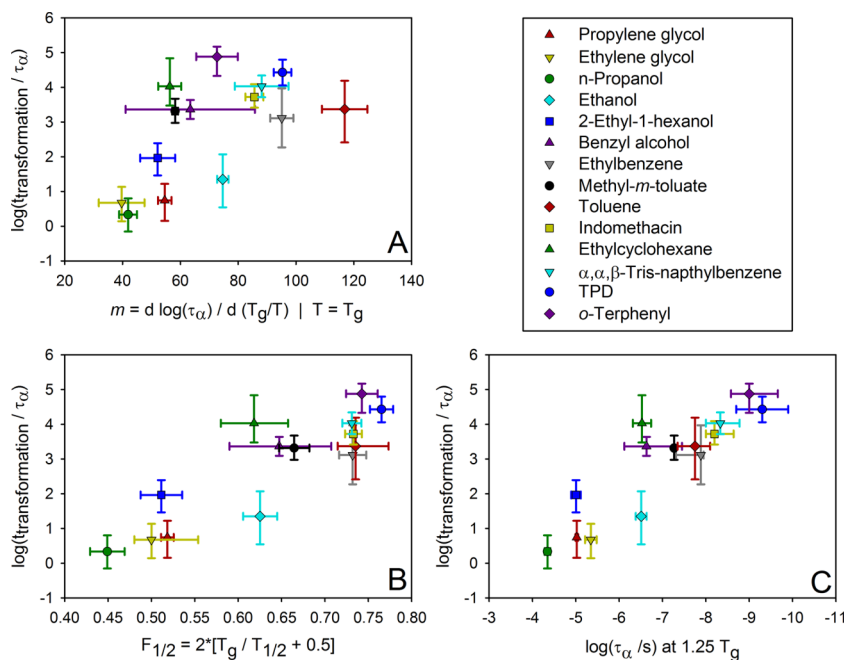


FIG. 8. Transformation times of 590 nm vapor-deposited glasses for 14 liquids, as a function of three different measures of supercooled liquid fragility. Data for the six alcohols are from this work. For the previously published data on eight other liquids, we use transformation front velocities for stable glasses deposited at $\sim 0.2 \text{ nm/s}$ and optimized $T_{\text{substrate}}$ ^{6,7,9,34,36,41,42} to calculate the transformation time for 590 nm films. In panels (b) and (c) we observe a moderate correlation between transformation times and fragility, as discussed in the text.

deposition is performed. In contrast, Figure 8 shows that the measures of fragility that are sensitive to higher temperature dynamics provide a better correlation.

Beyond the empirical correlations shown in Figure 8, we briefly describe two reasons why one might expect the stable glass forming ability to correlate with some measure of fragility. We understand the stable glass forming ability for a particular molecular system to be influenced by both the surface mobility at substrate temperatures below T_g and by the height of barriers for equilibrium configurations at these temperatures. As mentioned above, Chen and co-workers recently showed that fragility (measured by $\log(\eta)$ at $1.25 T_g$) correlates with enhancement of surface diffusion. They argue that the loss of neighbors at the surface can be thought of as an “excitation” similar to a temperature increase.⁴⁰ In this view, since bulk dynamics of low fragility molecules are less sensitive to temperature, these molecules should have less mobility at the surface. It is unknown if surface diffusion is precisely the relevant measure of the surface mobility for stable glass formation, but the argument by Chen and co-workers could also be extended to surface structural relaxation. A second reason why fragility might influence stable glass forming ability arises from the expected connection between fragility and barrier heights at low temperatures. For an equilibrium liquid at the strong limit of fragility, the barrier heights in the potential energy landscape do not increase at lower temperatures¹⁰⁵ (consistent with the Arrhenius temperature dependence for structural relaxation). Therefore, the ability to sample more configurations during vapor-deposition would produce a glass with the same-sized barriers as a liquid-cooled glass, and thus the vapor-deposited glass would not demonstrate any enhanced kinetic stability. In contrast, for a fragile equilibrium supercooled liquid, the barrier heights at equilibrium increase with decreasing temperature (as indicated by the non-Arrhenius temperature dependence for structural relaxation), with a greater rate of increase for more fragile systems. This reasoning leads to the expectation that more fragile systems potentially have more kinetic stability to gain through vapor deposition. While there is some debate as to whether fragile liquids continue to have non-Arrhenius dynamics in equilibrium near T_g ,^{106–108} configurations with higher barriers must be accessible via vapor deposition for otherwise glasses with high kinetic stability could not be obtained. At present, we view any relationship between fragility and stable glass forming ability shown in Figure 8 as an empirical observation that has a plausible rationalization. If the correlation shown in Figure 8(c) holds for future studies of vapor-deposited glasses, it will be desirable to sort out the role of the two contributions to stable glass forming ability that are described above.

Unstable glasses with decreased heat capacity

Vapor-deposited glasses of 2-ethyl-1-hexanol prepared at substrate temperatures below $0.90 T_g$ have the intriguing combination of an onset temperature below T_g , and reduced heat capacity. This combination has been observed previously for toluene and ethylbenzene glasses deposited near $0.60 T_g$.³⁴ We will briefly explain why we find this combination

surprising and how it might be interpreted. The heat capacity of glasses is attributed to vibrational modes, vibrational anharmonicities, and secondary relaxations.¹⁰⁹ A decrease in the glassy heat capacity could be explained by a shift in vibrational frequencies to higher frequencies, more harmonic vibrations, or by suppression of secondary relaxations. We can easily imagine that a liquid equilibrated at a lower temperature or a better packed glass would have all of these properties, and in addition have higher barriers to relaxation and thus increased kinetic stability. Thus we would expect that low molar volume, low heat capacity, suppressed beta relaxation, and increased kinetic stability would all be correlated in vapor-deposited glasses. These correlations hold for almost all the published literature for vapor-deposited glasses. For example, stable glasses have been found to have lower molar volumes than liquid-cooled glasses.^{1,12–15} The heat capacity decrease and the onset temperature increase have similar relationships with substrate temperature for vapor-deposited glasses of many molecules.^{6,8,9,16,20,23,34,36} Also, some previous investigations of unstable glasses produced at very low substrate temperatures have shown higher heat capacities (before going through an irreversible relaxation upon heating towards T_g).^{6,110,111} In contrast to these correlations which we regard as easy to explain, some vapor-deposited glasses of 2-ethyl-1-hexanol, toluene, and ethylbenzene have the seemingly contradictory combination of low kinetic stability (as indicated by rearrangements below T_g) and decreased heat capacity. This indicates that there must be regions of the potential energy landscape with low barriers that nevertheless are better packed in some respect. There is further evidence for such regions in a recent publication by Yu and co-workers.¹¹² They found that the secondary relaxation in toluene vapor-deposited glasses is suppressed compared to the liquid-cooled glass. While such a suppression would be expected (and is observed) for highly stable glasses, secondary relaxation was suppressed even for glasses deposited at very low substrate temperatures ($T_{\text{sub}}/T_g = 0.2$) that were likely unstable. Experiments combining calorimetry, dielectric spectroscopy, and vibrational spectroscopy on vapor-deposited glasses of a single system would further our understanding of the diversity of the states found in the potential energy landscape.

CONCLUSIONS

We have prepared glasses of six mono- and di-alcohols via physical vapor deposition to investigate how the presence of -OH groups might prevent stable glass formation. We investigated the properties of these glasses using AC nanocalorimetry. Quasi-isothermal annealing experiments were used to quantify the kinetic stability of the glasses. Benzyl alcohol forms a stable glass when deposited onto substrates near $0.85 T_g$, with transformation times that exceed $10^3 \tau_\alpha$; this is the first clear demonstration of an alcohol forming a highly stable glass via vapor deposition. Propylene glycol, ethylene glycol, and propanol form low stability glasses, showing transformation times that barely exceed those expected for a liquid-cooled glass. Ethanol and 2-ethyl-1-hexanol form moderate stability glasses. We speculate the

benzyl alcohol has higher surface mobility than the other alcohols and that this is the primary reason for its high stable glass forming ability.

Collectively, this series of vapor-deposited alcohol glasses shows a range of kinetic stabilities that has not previously been observed. Using these six alcohols and eight previously studied molecules, we have found a reasonably good correlation between kinetic stability and a recently proposed measure of fragility: $\log(\tau_\alpha)$ at $1.25 T_g$. This correlation is better than the correlation between kinetic stability and other measures of fragility ($F_{1/2}$ and m). We discussed why liquids with higher fragility might be expected to have higher stable glass forming ability, either through enhanced surface mobility or because configurations with higher energy barriers are present deeper in the potential energy landscape. We also used AC nanocalorimetry to compare the reversing heat capacity of the vapor-deposited glasses to liquid-cooled glasses. Consistent with previous work, glasses with high kinetic stability show decreased heat capacity. In a few cases, decreased heat capacity was also observed in glasses with low kinetic stability.

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